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Photopromoted Carbonylation of Alkyl Bromides Catalyzed by Copper Salts under Ambient Conditions

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Abstract: Photopromoted carbonylation of alkyl bromides with carbon monoxide or carbon dioxide catalyzed by copper salts can be carried out under ambient conditions (atmospheric pressure and room temperature) and the corresponding ester was produced. The yield and the selectivity of the ester can be improved greatly by addition of sodium phosphate.

Keywords: Photopromoted carbonylation, carbon monoxide, carbon dioxide, copper salts.

The synthesis of esters by carbonylation is an important and essential reaction, which usually requires high temperatures (150-200℃) and high pressure (10-20 MPa) or precious metal catalysts (Ru, Rh, Ir)[1]. There are many advantages, however, for photopromoted carbonylations such as ambient conditions and non-precious metal catalyst[2,3].

Carbon dioxide is a natural and inexpensive carbon source on our planet, to which much more carbon dioxide is produced by technical processes which have led to increasingly serious greenhouse effect. The conversion of carbon dioxide through chemical reaction is interesting from an environmental point of view, yet it is a challenge to chemists because of the highly thermodynamic stability of carbon dioxide. Its activation needs under severe reaction conditions, such as high pressure and high temperatures or with expensive catalysts[4]. Photocatalyzed activation and incorporation of carbon dioxide into organic compounds is one of the most attractive methods because of its mild conditions, inexpensive catalysts, decrease of CO_2 contamination. It is called an environmentally-friendly technique[3].

In previous paper, we have reported that the photopromoted carbonylation of alkyl halides with CO catalyzed by cobalt salts could be carried out under ambient conditions[5]. It is known that copper salts have not been used in photopromoted carbonylations of alkyl bromides as catalyst. We report herein use of copper salts as catalysts for the photopromoted carbonylation of alkyl bromides with CO or CO_2 under ambient conditions and the effect of Na_3PO_4 as additive on the reaction.

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Experimental

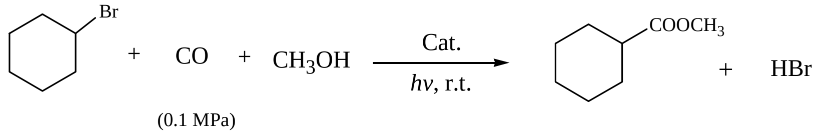
Carbon monoxide, carbon dioxide (99.9%, Dalian Guangming Institute); methanol (AP, Dalian Merro Stock Chemical Reagent and Glass Apparatus Co.); *n*-decane, bromocyclohexane, 1-bromooctane, 1-bromododecane (AP, Beijing Phentex Chemicals Co., Ltd.); copper chloride (AP, Beijing Hongxing Chemicals Co.); sodium phosphate, sodium biphosphate, copper sulfate, copper acetate, copper bromide, cuprous chloride (AP, Shenyang Chemical Reagent Co.); sodium methylate (AP, Shanghai Chemical Reagent Co.).

A typical reaction procedure was as follows: A quartz test tube containing a solution of alkyl bromides (100 mmol/L), catalyst (10 mmol/L) with Na_3PO_4, NaH_2PO_4 or NaOMe (30 mmol/L) as additive in methanol and under 0.1 MPa of CO or CO_2 pressure was irradiated for 25 hours by 400 W high pressure mercury lamp (GGY-400, Philips and Yaming Corp.) at room temperature. The quartz test tube was placed closely against the outer wall of the quartz reactor equipped with a 400 W high pressure mercury lamp and was cooled with circulating cold water to maintain room temperature. The reaction products were characterized by GC retention time and GC-MS.

Results and Discussion

The photopromoted carbonylation of bromocyclohexane with carbon monoxide and methanol catalyzed by copper salts can be carried out under ambient conditions, methyl cyclohexanecarboxylate was produced (**Scheme 1**). The results are shown in **Table 1**.

Scheme 1



Cat.= $CuCl_2$, $CuSO_4$, $Cu(OAc)_2$, $CuBr_2$, Cu_2Cl_2

Table 1 Effect of copper salts on carbonylation of bromocyclohexane with CO[a]

Catalyst	Conversion [b](%)	Yield (%)	Selectivity[c](%)
$CuCl_2$	100 (82)	66 (34)	66 (41)
$CuSO_4$	100 (83)	53 (23)	53 (28)
$Cu(OAc)_2$	100 (84)	48 (19)	48 (23)
$CuBr_2$	95 (77)	40 (13)	42 (17)
Cu_2Cl_2	98 (80)	57 (32)	58 (40)

a: Cat.:Na_3PO_4 = 1:3(1:0) (molar ratio), b: Bromocyclohexane, c: Selectivity (%) = Yield / Conversion × 100%.

The results indicated that with $CuCl_2$ as catalyst methyl cyclohexanecarboxylate was obtained in 34% yield and with selectivity of 41%. Cyclohexene and cyclohexane were the major byproducts of this reaction. The yield of the ester can be increased from 34% to 66% and the selectivity improved from 41% to 66% by addition of Na_3PO_4.

The role of Na_3PO_4 could be assumed as a base to neutralize hydrogen bromide formed in the reaction[6]. For comparison we used NaH_2PO_4 as additive. The result showed that the yield of the product was only 17%. It was suggested that the acidic additive is disadvantageous compared with the basic additive of Na_3PO_4. Strong basic additive, such as NaOMe gave somewhat lower yield (58%) and selectivity (62%) as compared to yield (66%) and selectivity (66%) with Na_3PO_4 as additive. We found that the optimum conditions for this reaction were $CuCl_2$ as catalyst and Na_3PO_4 as additive. Furthermore it is indicated in **Table 1** that Cu (Ⅱ) gave slightly higher yield for methyl cyclohexanecarboxylate than Cu (Ⅰ) did.

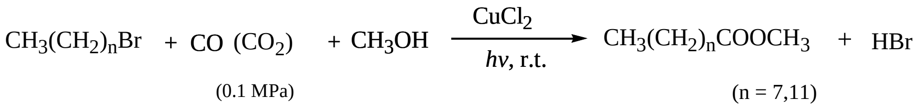
In addition an effort was made to use CO_2 as carbon resource. The results are shown in **Table 2**.

Table 2 Effect of copper salts on carbonylation of bromocyclohexane with CO_2[a]

Catalyst	Conversion[b] (%)	Yield (%)	Selectivity (%)
$CuCl_2$	94	34	36
$CuSO_4$	94	33	35
$Cu(OAc)_2$	94	32	34
$CuBr_2$	88	28	32
Cu_2Cl_2	94	33	35

a: Cat.: Na_3PO_4 = 1:3 (molar ratio), b: bromocyclohexane.

Scheme 2



$$\underset{}{CH_3(CH_2)_nBr} + \underset{(0.1\ \mathrm{MPa})}{CO\ (CO_2)} + CH_3OH \xrightarrow[h\nu,\ \mathrm{r.t.}]{CuCl_2} \underset{(n = 7,11)}{CH_3(CH_2)_nCOOCH_3} + HBr$$

The results indicated that photopromoted carbonylation of bromocyclohexane with CO_2 catalyzed by copper salts and using Na_3PO_4 as additive could also be taken place under ambient conditions. But both of the activity and the selectivity for carbonylation are lower than that of CO. If the reaction was carried out without Na_3PO_4, only gave 21% yield. It means Na_3PO_4 could improve the carbonylation of CO_2. Other copper salts with Na_3PO_4 could also catalyze the carbonylation of bromocyclohexane with CO_2 to give slightly lower yield. It is found in our previous research[3] that acetone was essential in the carbonylation of carbon dioxide with cobalt salts as catalysts and the reaction could hardly be completed in absence of acetone. However, with copper salts as catalysts the carbonylation of alkyl bromides with carbon dioxide could also be completed without acetone. The photopromoted carbonylation of 1-bromooctane and 1-bromododecane can take place under the same conditions (**Scheme 2)**. The results are shown in **Table 3**.

It can be seen that CO is more active than CO_2 and the former gave 80% yield of the ester as compared to 26% yield given by the latter, when using 1-bromooctane as the substrate and the major byproducts were 1-octene and octane. And photopromoted carbonylation of 1-bromododecane with CO and CO_2 gave 24% yield and 8% yield of $CH_3(CH_2)_{11}COOCH_3$, respectively and the major byproducts were 1-dodecene and dodecane. It could be concluded that $CuCl_2$ can effectively catalyze photopromoted carbonylation of alkyl bromides by using Na_3PO_4 as additive, carbon monoxide or carbon dioxide as carbon resource under ambient conditions. Further research on mechanism is underway.

Table 3 Results of carbonylation of 1-bromooctane and 1-bromododecane with CO or CO_2[a]

Substrate	Gas	Conversion[b] (%)	Yield (%)	Selectivity (%)
1-bromooctane	CO	98	80	82
	CO_2	84	26	31
1-bromododecane	CO	76	24	32
	CO_2	46	8	17

a: Cat.: Na_3PO_4 = 1:3 (molar ratio), b: alkyl bromides.

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